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Reaction of Bisphenol-A-Diglycidyl Ether (BADGE) from Can Coatings with Food Components

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Introduction

The internal coating of cans may release rather large amounts of epoxy compounds into the packed food. In 1996, throughout Europe up to several tens of mg/kg of Bisphenol-A-diglycidyl ether (BADGE) were found in oily foods like fish in oil, meat or sauces (1, 2). While the migration of BADGE was substantially reduced in the mean time (3–7), many related components, such as of the novolak glycidyl ethers (NOGE) (8, 9) and BADGE monoreaction products (one of the glycidyl groups reacted with, e.g., a phenol, alcohol or carbonyl compound (10, 11)) are still not under satisfactory control. Most of the migrating material has not even been identified.

Migrating epoxy compounds are likely to react with food components, promoted by the fact that most of the transfer occurs during heat treatment, such as sterilization. In aqueous foods (e.g. canned vegetables, fruits, raviolis or soups), the most obvious reaction is hydrolysis, resulting in the diol. The kinetics of this reaction in simulant liquids has been studied (12–14). Reaction with chloride ions in foods or gastric fluids was also shown in simulants (15).

As the solubility of BADGE in water ist low, reactions depend on the food properties. Oil or fat keep BADGE out of the aqueous phase and protect the epoxy group from hydrolysis or other reactions with components in the aqueous phase. This explains why often little hydrolyzed BADGE is found in products like fish in oil. As long as the oily phase consists of fairly large spheres, even attack by hydrochloric acid is slow, but more intense mixing, i.e. splitting of the droplets to smaller units, strongly accelerates the reaction (1). This observation is important in the con-

text of the question whether or not BADGE passes through the stomach unchanged: fat or oil protecting BADGE in the canned food also seem to protect it in the stomach.

It seems a rather plausible hypothesis that BADGE and related epoxy compounds would also react with food components other than water and chloride since the latter are unlikely to be the most reactive components. This is of interest, firstly, because the migration might be underestimated and, secondly, because there could be toxic compounds among these reaction products. The problem has been observed with many direct or indirect food additives, but the extent by which BADGE «disappears» in some foods seems unparalleled.

«Disappearance» means that the BADGE added to a food is no longer detected, neither as such nor as (identified or non-identified) other peaks in the chromatographic windows investigated.

Experimental

Samples

The main experiments were performed on peas, corn, tomatoes, and tuna. Deep frozen, non-salted peas and salted (0.9 %) sweet corn were bought in bags which did not release material producing peaks in the chromatographic experiments. One of the two tomato products and the tuna in water contained 1 g/100 g of salt, while the other tomato product was unsalted. They were from cans, but were selected to contain less than 30 µg/kg of BADGE-related material. The tuna in water contained less than 2 % fat.

Before homogenization, an equal amount of water was added to tuna, sweet corn and peas in order to obtain a fairly stable suspension. For tomatoes, a similar suspension was obtained without addition of water.

Analytical methods

The analytical methods were previously published (16). Normal phase HPLC (NPLC) involved extraction of the homogenate into methyl-tert.-butyl ether (MTBE), acetylation with pyridine/acetanhydride and chromatography on a cyano phase with a pentane/MTBE/1-propanol gradient and fluorescence detection (FD) at EX 225 nm/EM 295 nm. Reversed phase HPLC (RPLC) was performed after adding ethanol to the food homogenate and centrifugation, using a C8 silica, an ethanol/water gradient and also FD. Peaks from NPLC were identified or confirmed by GC-MS with large volume (100 µl) on-column injection (11).

Reaction with food components

Simulation of stomach conditions

Aqueous solutions (50 ml) containing 0.9 % NaCl and 0.1 % formic acid as a buffer were adjusted to pH 1.2, 3 or 4 by dilute hydrochloric acid or sodium hydro-

xide solutions. BADGE was added at 4 mg/l using a stock solution of 1 mg/ml in dioxane. Solutions were thermostated at 37 °C in an oven. Samples of 2 ml were taken after 45, 110, 120 min as well as 22 h. Reactions were stopped by extraction with MTBE. Extracts were acetylated and analyzed by NPLC. The same experiments were performed with a homogenate of sweet corn to which 0.9 % NaCl and BADGE were added. The pH was adjusted without a buffer.

Results were expressed as percentages of the BADGE-related material recovered, neglecting the fact that a minor amount of BADGE «disappeared».

Reaction with salt; «disappearing» BADGE

Various amounts of BADGE in dioxane and components to test reactions were added to 10 g of food homogenate containing 5 ml of water in an Erlenmeyer. BADGE concentrations in dioxane were 1 to 100 mg/ml, such that the final test mixtures did not contain more than 1 % of dioxane. After shaking, the samples were allowed to stand at ambient temperature or in an oven at 90 °C. To simulate sterilization, 5 g samples of food homogenates with the components of interest added were enclosed in a 10 ml autosampler flask and heated at about 120 °C in a pressure cooker containing some water.

Results

Reaction with chloride ions

Reaction of BADGE with chloride ions was of interest because the resulting chlorohydrins are considered as potential carcinogens. It may take place in the salted canned food (primarily during sterilization or hot filling) or in the hydrochloric acid of the stomach.

Gastric fluid simulation

Table 1 shows the conversion of BADGE at 37 °C in water and sweet corn homogenate after addition of 0.9 % sodium chloride and pH adjustment (1.2 to 4).

At a pH of 1.2, the conversion in water was virtually complete after less than 110 min (after 45 min, 3 % of BADGE was left). The concentrations of the dihydrolyzed BADGE (BADGE.2H_2O, structure in, e.g., (16)) and of BADGE reacted with HCl on both glycidyl groups (BADGE.2HCl) were equal (25 %). The concentration of the mixed reaction product (BADGE.HCl.H_2O) reached 50 %. This indicates that at 0.9 % salt in water, the conversion to the chlorohydrin and to the hydrolysis products proceeds at the same yields.

At pHs of 3 or 4 (conditions in the stomach of rats or in a human stomach after a heavy meal), the reaction was far slower. After 260 min, only a minor part of the epoxy groups was converted, primarily to the monoreaction products (BADGE.HCl and BADGE.H_2O). After 22 h, still 6 % BADGE was left at a pH of 3 and even 32 % at a pH of 4.

Table 1

Conversion of BADGE (4 mg/l) in water or sweet corn homogenate after addition of 0.9 % salt and pH adjustment (1.2 to 4). Distribution as weight percent of the resulting mixture

	Water (9 g/kg salt)						Sweet corn homogenate (19 g/kg salt)					
pH	*BADGE*	*.HCl*	*.H_2O*	*.2HCl*	*.2H_2O*	*.HClH_2O*	*BADGE*	*.HCl*	*.H_2O*	*.2HCl*	*.2H_2O*	*.HClH_2O*
Reaction time 110 min												
1.2	< 1	< 1	< 1	24	25	50	10	16	3	27	8	36
3	82	10	8	< 1	< 1	< 1	95	3	2	< 1	< 1	< 1
4	89	6	5	< 1	< 1	< 1	93	4	2	< 1	1	< 1
Reaction time 260 min												
1.2	< 1	< 1	< 1	24	26	51	< 1	2	4	40	10	44
3	55	18	19	2	3	3	89	8	3	< 1	< 1	< 1
4	78	12	10	< 1	< 1	< 1	87	8	4	< 1	1	< 1
Reaction time 22 h												
1.2	< 1	< 1	< 1	25	25	50	< 1	< 1	3	40	10	47
3	6	19	17	13	15	29	61	25	7	6	1	1
4	32	29	21	7	2	9	64	16	8	4	3	5

At the pH of 3, concentrations of BADGE.HCl and BADGE.H_2O, as well as of BADGE.2HCl and BADGE.$2H_2O$ were again similar, confirming that at 0.9 % salt the probability of reacting with chloride and water is almost identical. At a pH of 4, the formation of the chlorohydrins was favored, as clearly seen after 22 h reaction time. This suggests that at lower proton concentration the reaction speed decreases less for chloride than for water. In conclusion, at pHs between 1.2 and 4 the reaction kinetics with chloride is more than two orders of magnitude faster than the hydrolysis and this difference increases at higher pH.

The reaction performed in homogenized sweet corn was substantially slower, presumably because adsorption on the solids partially protects BADGE from the aqueous phase. Furthermore, reaction towards the chlorohydrin was favored because the sweet corn contained 1 % of salt.

Reaction with salt in foods

Results shown in table 2 refer to homogenized foods to which about 10 mg/kg of BADGE and various amounts of salt had been added (admixed salt being added up with that labelled). The pH was left unchanged. Reaction occurred either during 1 day at 25 °C or during 30 min at about 120 °C in a pressure cooker in order to simulate sterilization.

In the tomato homogenate reacting at ambient temperature, only small amounts of monoreaction products (BADGE.HCl and BADGE.H_2O) were found. The formation of BADGE.HCl was strongly accelerated upon increasing the salt concentration from 1.0 to 4.0 %.

Treatment at 120 °C converted most BADGE. With 1.0 % salt, 75 % of the recovered material consisted of BADGE.$2H_2O$, which is more than found in table 1. Formation of BADGE.2HCl rapidly increased with higher salt concentrations and reached 60 % BADGE.2HCl at 4.0 % salt.

«Disappearing» BADGE

BADGE concentrations found in the MTBE extracts decreased more rapidly than reaction products with water and hydrochloric acid were recorded. Extraction yields typically ranged between 75 and 95 %, occasionally being as low as 60 % (16). Hence, a substantial proportion of the 27–36 % of material missing in the tomato homogenate could correspond to the extraction losses.

With peas, the composition of the reaction products was similar to the one observed in sweet corn, but about 85 % of the BADGE added had «disappeared». This clearly exceeded the losses during extraction. Analogous results were obtained with tuna in water, but well 98 % of the BADGE added «disappeared» after a simulated sterilization with 2 % salt.

Table 3 shows results obtained for different food types and BADGE additions. Even for pineapples and tomatoes (unsalted product, different from that used above), a substantial part of BADGE «disappeared», but clearly less than for peas and

Table 2

Recovered BADGE and BADGE reaction products from homogenates of tomatoes, peas and tuna to which BADGE and salt had been added. % Material «disappeared», 100 % minus recovered material

NaCl	*Treatment*		*Recovered products (% referring to the BADGE added)*						*% Material*
(%)	*time*	*temp. (°C)*	*BADGE*	*.H_2O*	*.HCl*	*.HCl.H_2O*	*.2HCl*	*.$2H_2O$*	*«disappeared»*
Tomatoes									
1.0	1 d	25	68.6	2.3	0.6				28.6
1.9	1 d	25	62.9	2.3	1.8				33.0
4.0	1 d	25	51.4	1.7	11.4				35.5
1.0	30 min	120	3.6	4.6		10.3	1	44.6	36.0
1.9	30 min	120	2.5	2.3	2.8	21.7	6.9	31.4	32.4
4.0	30 min	120	1.1			24.6	43.4	4.2	26.6
Peas									
0.3	30 min	120	3.1			2.3		6.3	88.3
0.9	30 min	120	3.1			3.7	0.8	5.4	86.9
3.0	30 min	120	2.3			6.6	8.1	1.8	81.2
Tuna in water									
1.3	1 d	25	25.0		2.0			1.3	71.6
2.0	1 d	25	15.4		2.5			1.3	80.9
2.0	30 min	120						1.8	98.2
4.0	30 min	120				3.2	1.6	3.1	92.0

Table 3

Recovered BADGE reaction products after addition of various concentrations of BADGE to food homogenates. Sum .MT, sum of the methylthio derivatives

	BADGE (mg/kg)	°C	Time (h)	Recovered (% of BADGE added) .H_2O	.HCl	.HCl.H_2O	.2H_2O	Disappeared (%)	Sum .MT
Pineapple	10	90	15				36	64	
Tomato	10	90	15			8	29	63	
Peas	440	120	2	< 0.5		< 0.5	16	84	1.4
Tuna	19	120	2			0.5	2.5	97	4.7
	100	90	15			0.9	2.2	97	4.0
	580	120	2			0.7	2.5	97	3.4
	900	120	2			0.9	2.4	97	3.5

tuna. Addition of a far larger amount of BADGE to peas (440 mg/kg) caused a «disappearance» in the same range as for 10 mg/kg, indicating that the material reacting with BADGE is not a trace component which is rapidly exhausted. The same was observed for tuna, where the percentage of BADGE recovered as $.2H_2O$ and $.HCl.H_2O$ remained constant regardless of the initial BADGE concentration (19 or 900 mg/kg). No higher additions were tested since solubility of BADGE is a problem. Mediator solvents interfere with the reaction and if BADGE is precipitated, it tends to polymerize (as concluded from analysis by size exclusion chromatography).

Methylthio derivatives of BADGE

To explain the «disappearance» of BADGE, the chromatograms from NPLC-FD, RPLC-FD and GC-MS were searched for reaction products of BADGE with food components. Nearly all BADGE reaction products show a similar response on FD. The high selectivity of FD and the relatively large amounts of BADGE added resulted in chromatograms virtually free of signals from food components, which should have facilitated the detection of reaction products corresponding to at least 1 % of the BADGE added.

NPLC of the acetylated extracts from some foods revealed at least one of the extra peaks shown in figure 1 (specified by .MT) for homogenized tuna in water spiked with BADGE. The eluates corresponding to the peaks were collected and analyzed by GC-MS using large volume on-column injection.

The mass spectrum of the predominant peak, designated $BADGE.MT.H_2O$, is shown in figure 2. Apart from m/z 43 (acetyl), the spectrum shows two main fragments at m/z 147 and 159. The signal at m/z 159 is from the acetylated diol side

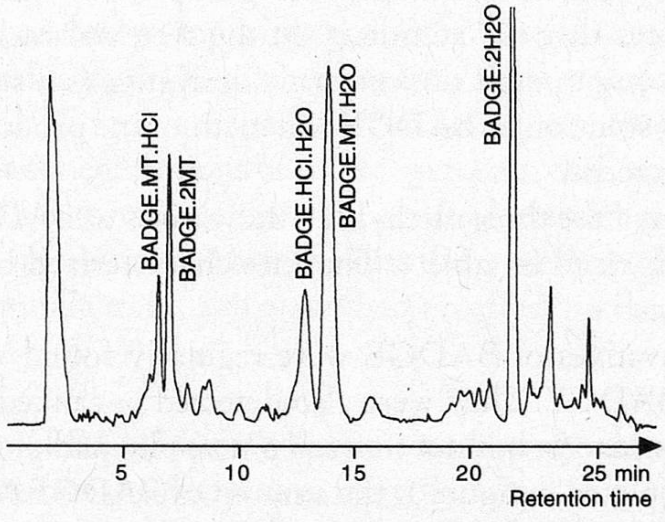

Figure 1 **NPLC-FD chromatogram from tuna in water spiked with 10 mg/kg of BADGE and heated at 90 °C overnight. The sum of all peaks corresponds to 7 % of the BADGE added. MT, methylthio**

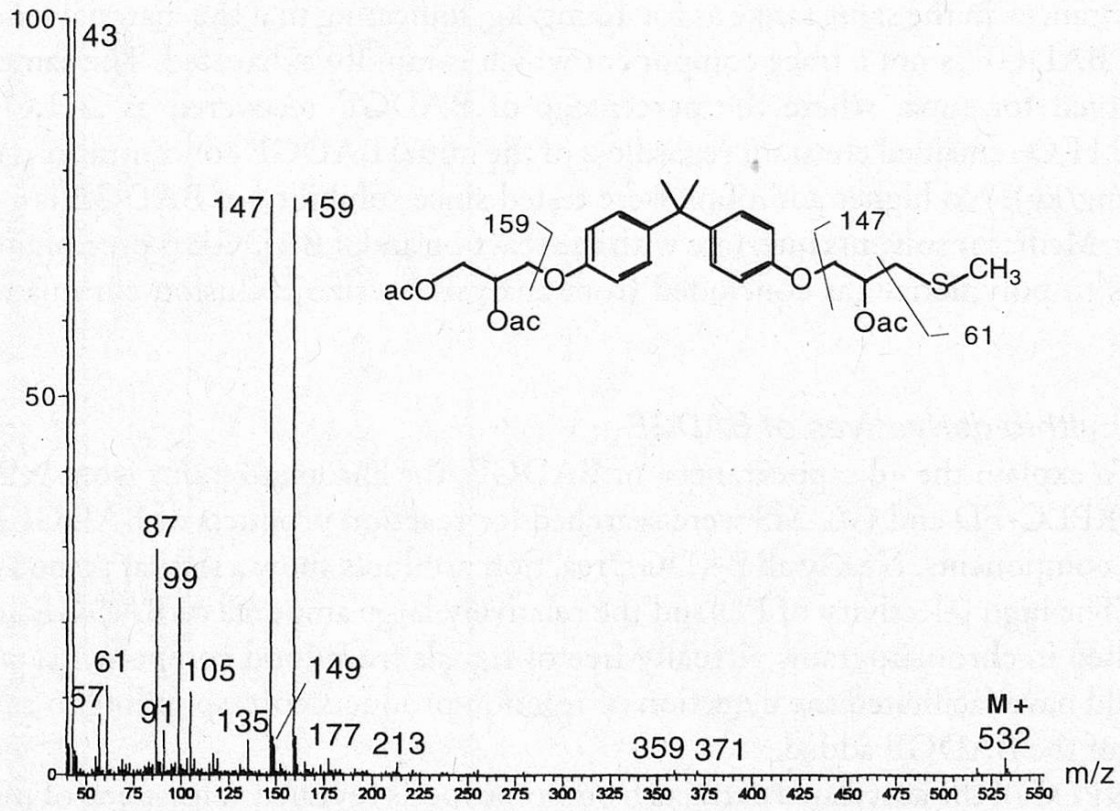

Figure 2 **Mass spectrum (EI) of BADGE with a methylthiol group added on one glycidyl ether and with water on the other (BADGE.MT.H_2O) after acetylation**

chain; m/z 147 was interpreted as the (acetylated) methylthio derivative of the glycidyl group. The signal m/z 149 resulting from the ^{34}S isotope has the expected intensity and m/z 105 results from the side chain after loss of the acetyl group. The fragment m/z 61 corresponds to the methylthio group with a methylene of the side chain, which indicates that the sulfide is on the terminal carbon of the glycidyl group and that the compound is the «normal» derivative (see structure in figure 2). Heating an aqueous solution of BADGE and methionine produced this compound at a yield of a few percent.

The mass spectra of the three methylthio derivatives of BADGE detected in spiked foods are summarized in table 4. They are characterized by the signals of the acetylated side chains.

Methylthio derivatives of BADGE were regularly found when tuna in water was warmed with BADGE. They were also detected in canned plums, pineapples, peaches, peas and tomatoes, but not in fresh pineapples and plums.

In the sample depicted in figure 1, the amount of BADGE.MT.H_2O corresponded to 2.8 % of the BADGE added, BADGE.2MT to 1.1 % and BADGE.MT.HCl to about 0.3 %. They represented more than twice the concentration of BADGE.2H_2O plus BADGE.HCl.H_2O. Most samples contained BADGE.MT.H_2O as the only methylthio derivative and concentrations were somewhat lower.

Table 4
Mass spectra of acetylated methylthio (MT) BADGE derivatives (% abundance)

Compound	*M+*	*Fragments*
BADGE.2MT	520 (3)	147, 43 (65), 87 (45), 99 (20), 61 (20), 105 (20), 91 (12)
BADGE.MT.H_2O	523 (3)	43, 147 (80), 159 (75), 87 (30), 99 (20), 61 (15), 105 (15)
BADGE.MT.HCl	508 (2)	43, 135 (85), 147 (80), 87 (45), 99 (20), 105 (20), 61 (15)

Up to 20 mg/kg of BADGE methylthio derivatives were found in heavily spiked tuna, suggesting that the precursor was not a trace component and that the reaction was controlled by relative reaction rates rather than by the concentration of the precursor present in the sample.

The source of the methylthio group was not identified. Methyl mercaptane was not considered as a candidate because of its intense odor. An attempt to produce the derivatives with dimethyl disulfide failed. The reaction with methionine gave a low yield and it cannot be ruled out that the reaction occurred with an impurity.

Unsuccessful search for further reaction products

As the peaks found in the chromatograms explained only a few percent of the «disappeared» BADGE, the following experiments were performed. Possible bonding to proteins was investigated by reacting tuna with large amounts of BADGE followed by hydrolysis with concentrated HCl. The resulting mixtures were analyzed directly by RPLC, or derivatized with ethylchloroformiate and analyzed by NPLC and GC-MS. Alternatively they were acetylated or silylated. No peak corresponding to at least 1 % of the BADGE added was detected.

Reactivity of some important food components with BADGE was tested by addition at high concentrations to foods together with 10 mg/kg of BADGE. It was hypothesized that food components like proteins or metals could catalyze the reaction of BADGE. Addition of 100 g/kg of sugar to fresh pineapple had no effect on the result (most BADGE recovered as BADGE.2H_2O, no new peaks in NPLC-FD after acetylation). At concentrations of several percents, carboxylic acids did not react with BADGE to a detectable extent – they just accelerated hydrolysis. Addition of alanine, cysteine, methionine, dimethyldisulfide, methyl ethyl sulfide, phenylthioethanol and ammonia to tuna in water had no effect on the results.

Discussion

«Disappearance» of BADGE may be explained by several ways:

1. MTBE did not extract the derivatives from the foods (high polarity).
2. The derivatives were not eluted within the HPLC or GC windows looked at – although NPLC and RPLC were performed with broad gradients opening a wide window.

3. The derivatives were not detected in HPLC-FD because the chromophore was modified.
4. BADGE was bonded to solids or macromolecules.
5. BADGE reacted with such a large number of components that the resulting peaks were not detectable.

There is not sufficient evidence to confirm any of these hypotheses, but the combination of the last two seems most plausible.

How to check migration into foods?

Control by the trade and the public authorities usually has no means to check the migration of, e.g., BADGE other than through the analysis of the canned foods. The following scenario is likely to be rather frequent. In an aqueous product, the analyst finds a modest amount of the hydrolyzed component and assumes that this represents the migrated BADGE. As the presence of BADGE.$2H_2O$ is not considered as alarming, he or she files the result among those of no concern.

It is really true that the BADGE.$2H_2O$ found represents the migrated material? For tuna in water, merely 3 % ot the BADGE added was recovered as BADGE.$2H_2O$ and BADGE.HCI.H_2O, meaning that migration could be underestimated by a factor as high as 30. For instance, 0.2 mg/kg of BADGE.$2H_2O$ is hardly of direct concern. However, if 30 times more BADGE has migrated (6 mg/kg), the conclusion will be entirely different.

The toxicity of BADGE and BADGE.$2H_2O$ has been investigated, but nothing is known about the toxicity of the 97 % of undetected (unidentified) material.

The interpretation of the analytical result leaves open a wide range of hypotheses. There is, for instance, no certainty that reactions in real canned foods proceed in the same way as in our spiked foods. If reactions of BADGE take place already in the coating, there might be no opportunity for BADGE to react with the food. BADGE.$2H_2O$ may, furthermore, be present in the coating as such or released by the hydrolysis of lacquer components other than BADGE.

Implications of the reaction with foods

It is not really a surprise that BADGE reacts with food components other than water and salt (and is, of course, not the first chemical known to behave in this way). Water is usually present as the most abundant component, but it is not a particularly reactive compound for an epoxy group. Chloride, for example, reacts several hundred times faster.

Specialists know for quite some time that canned products containing BADGE at concentrations exceeding the legal limit just need to be stored for a sufficient amount of time before being sold: in oily foods, such as fish in oil, we found that the BADGE concentration typically decreases by a factor of 10 at least per year. Hydrolysis only accounts for a minor part of the BADGE elimination and, hence, it re-

mains unknown it which form the «disappeared» BADGE is ingested by the consumer.

We repeatedly found indications that thorough mixing of food samples (e.g. fish in oil) reduced the BADGE concentrations. Since hydrolysis is not substantial even over a full day, it cannot account for the losses observed – but components with a far higher reactivity than water could.

Conclusions for the legislators

Legislators are called upon to find ways to ensure safety of food products. If as much as 97 % of the migrating BADGE can react with food components other than water and chloride, the toxicity of up to 97 % of the material really ingested cannot be assessed. It is unlikely that chloride is the only food component producing a potentially cancerogenic derivative of BADGE.

Legislators may impose limits for migration into simulants, arguing that a coating releasing no BADGE into the simulant does not create the above problems. However, today at least this is not a viable solution for the control by the trade or the public authorities since it is mostly impossible to get hold of the unused cans.

Legislators should consider at least the following three conclusions:

- For reactive substances, migration tests should be supplemented by a determination of their fate: detectable derivatives must be identified and the proportion of «disappeared» material measured.
- As long as the derivatives of a migrant are identified incompletely, a factor should be assessed that relates the detected derivatives to the migration of the mother compound (e.g. a factor of 30 for BADGE in tuna in water when referring to BADGE.2H_2O and BADGE.HCl.H_2O).
- As long as neither the amount of migration nor the toxicity of the «disappeared» material can be assessed, legal limits for foods must be set low enough to include a safety margin accounting for the unknown risks.

Summary

97 % at least of BADGE added to tuna in water «disappeared», i.e. was no longer detectable neither as BADGE nor as hydrolysate or HCl-derivative. Hence, when determined through known derivatives, the migration may be underestimated by a factor of more than 30, and the toxicity of more than 97 % of the material remains out of control.

In several foods, a few percents of the BADGE added were converted to methylthio derivatives. No other reaction products were identified, presumably because they are excessively numerous.

Bonding of reactive migrants to food components and their «disappearance» should be tested before setting legal limits. The limits must, furthermore, be sufficiently low to account for related unknown risks.

Zusammenfassung

Nach Zugabe von BADGE zu Tunfisch in Wasser «verschwanden» mindestens 97 % des beigefügten Materials, d.h. es war weder als BADGE noch als Hydrolysat oder HCl-Derivat nachweisbar. Mit der Analytik der bekannten Derivate könnte die Migration also um einen Faktor von mindestens 30 unterschätzt werden und die Toxizität von über 97 % des Materials unüberprüft bleiben.

In manchen Lebensmitteln wurden einige Prozente des zugegebenen BADGE zu Methylthioderivaten umgesetzt. Weitere Reaktionsprodukte liessen sich nicht identifizieren, vermutlich weil ihre Anzahl unüberschaubar gross ist.

Die Bindung reaktiver Migratkomponenten an Lebensmittelbestandteile und das Ausmass des «Verschwindens» sollten überprüft werden, bevor gesetzliche Limiten festgelegt werden. Schliesslich müssen die Limiten genügend tief sein, um derartige Risiken zu berücksichtigen.

Résumé

Après un ajout de BADGE dans un homogénat de thon à l'eau, 97 % au moins du BADGE «disparaît», ce qui signifie qu'il n'était plus détectable en tant que BADGE, hydrolysat ou dérivés HCl. Lors de l'analyse des dérivés connus, le taux de migration peut donc être sous-estimé d'un facteur de plus de 30 et la toxicité de plus de 97 % des composés reste inconnue.

Dans certains aliments, un faible pourcentage du BADGE a été converti en dérivé methylthio. Aucun autre produit de réaction n'a pu être identifié, probablement en raison du grand nombre de dérivés possibles.

La liaison des migrants réactifs avec des composés des aliments ainsi que l'ampleur de la «disparition» doivent être étudiés avant la fixation de limites légales. Ces limites doivent être suffisamment basses pour tenir compte des risques inconnus.

Key words

Bisphenol-A-diglycidyl ether (BADGE), Canned foods, Reaction of migrants with food, Chlorohydrins of BADGE

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